PREPARATION OF Pd/CARBON AND Pt-Pd/CARBON NANOPARTICLE METAL ALLOY CATALYSTS BY SUPERCRITICAL FLUID DEPOSITION

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Abstract

The preparation of Pd and Pt-Pd nanoparticle binary metal alloys on carbon support BP 2000 by the supercritical CO_2 deposition method was investigated. The carbon supports were first impregnated with dimethyl (cyclooctadiene) platinum ($PtCODMe_2$) from the supercritical CO_2 solution and the resulting composites were converted to Pt/C composites by thermal reduction under H_2/N_2 atmosphere at 200 ^{o}C for 4 hours. Then the Pt/C composites prepared were deposited with $Pd(acac)_2$ in supercritical CO_2. Chemical reduction in supercritical CO_2 with hydrogen was used to obtain PtPd/C. The catalysts were characterized by using X-ray diffraction (XRD). Thermodynamics and kinetics of adsorption of $Pd(acac)_2$ on BP2000 support was also investigated. The adsorption isotherm was measured at 3000 psi and 60 ^{0}C and was represented by a linear model. The factors influencing the formation of Pd and PtPd binary nanoparticles including reduction temperature, precursor loading and hydrogen concentration were investigated.

Introduction

Supported metal nanocomposites which include metal particles with diameters between 1-100 nm dispersed on a high surface area substrate have attracted a great deal of interest. Metal nanoparticles have potential applications including optical, electronic, magnetic devices and catalysis [1]. High surface area carbon substrate supported metal nanoparticles are widely used as catalysts for many reactions. Many studies [2, 4, 5, 6, 7, 8, 9, 10, 11] have been conducted in order to investigate the preparation of supported metal nanoparticles. There are several methods to synthesize these nanoparticles which include impregnation, chemical vapor deposition, sol-gel processing, deposition-precipitation, microemulsion generation using organic stabilizing agents. Control over particle size, distribution and metal composition in the composites is challenging using these methods [12].

Supercritical deposition is an alternative and promising way to prepare catalysts. This process involves the dissolution of a metallic precursor in a supercritical fluid and the exposure of a porous support to the solution. After adsorption of the precursor on the support, the metallic precursor is converted to its metal form by chemical or thermal reduction. This promising catalyst preparation technique results in small particle sizes and homogeneous dispersions. An additional advantage of this technique is the ability to thermodynamically control the metal loading.

Carbon supported palladium catalysts are used in a wide range of reactions, especially for hydrogenation in the fine chemical industry [13]. They are used in the gas phase hydrodechlorination of dichloromethane [14], hydrogenation of 2-butyne-1,4-diol in propan-2-ol [15], hydrogenolysis of hydroxymatairesinol [16] and lactose oxidation to produce lactobionic acid [17]. In this study, supercritical CO_2 deposition was used to prepare carbon supported Pd and Pt-Pd nanoparticles. The scheme involved the adsorption of palladium acetylacetonate ($Pd(acac)_2$) as the organometallic precursor onto porous carbon support surface (Black Pearl 2000, Cabot International) and reduction of the precursor on the support with H_2 in scCO2 at the given experimental conditions.

The study consists of two parts. In the first part, adsorption isotherm of $Pd(acac)_2$ on carbon support (Black Pearl-BP 2000) at 3000 psi and 60 ^{0}C was obtained. BP 2000 is a high surface area carbon

substrate with the following surface and structural parameters: standard BET surface area: 1450 m^2/g, external surface area: 515 m^2/g, micropore volume: 0.454 cc/g and total pore volume: 1.75 cc/g [18]. The adsorption isotherm is crucial in order to understand the equilibrium relation between the concentration of adsorbent in the scCO$_2$ phase and the amount adsorbed on carbon substrate. After the determination of the adsorption isotherm, a kinetics model was developed for adsorption at the given experimental conditions.

In the second part of the study, the factors influencing the formation of Pd and PtPd binary nanoparticles including reduction temperature, precursor loading and hydrogen concentration were investigated.

Materials & Methods

Palladium (II) acetylacetonate (99 %) was purchased from Aldrich. Black Pearl 2000 was purchased from Cabot International. The chemicals were used as received. Carbon dioxide (99.998 %) was purchased from Messer Aligaz.

The vessel used for adsorption and reduction experiments was a 54 mL stainless steel vessel which is fitted with two sapphire windows (1 in. in diameter, Sapphire Engineering, Inc., Pocasset, MA) sealed on both sides of the vessel with polyetheretherketone O-rings (Valco Instruments, Inc., Houston, TX), a thermocouple assembly, a vent line and a rapture disk assembly (Autoclave Engineers). The experimental set-up is given in Figure 1. For the adsorption isotherm experiments, a certain amount of organometallic precursor (palladium (II) acetylacetonate) (Pd(acac)$_2$), a certain amount of substrate (BP2000) in a pouch and a stirring bar were placed into the vessel for each run. The vessel was heated to 60 ^{o}C by a circulating heater/cooler (Cole Parmer, Model 12108-15). Then it was pressurized with CO$_2$ from a syringe pump (Teledyne Isco, Model 260 D) to a pressure of 3000 psi. A yellow solution of fluid phase was observed from sapphire windows which indicated that the organometallic precursor was dissolved in supercritical CO$_2$. During the adsorption process, the Pd(acac)$_2$ dissolved in the fluid phase adsorbed onto the substrate. The system was kept at 3000 psi and 60 ^{o}C in batch mode until equilibrium was reached which took around 3 hours for each run. Then, the solution in the vessel was drained slowly through the vent line into the hood. The vessel was cooled and the impregnated substrate was removed from the vessel. The amount of Pd(acac)$_2$ adsorbed into the substrate was determined by the weight change of the substrate using an analytical ballance accurate to $\pm$ 0.1 mg (AND GR-200).

For the reduction of the Pd(acac)$_2$/BP 2000 composites, a 10 ml of solution of H$_2$ in CO$_2$ (PH$_2$=8 bar, P$_{Total}$=3000 psia) was injected using the syringe pump. It was observed that, after a short time H$_2$ was injected, the yellow solution turned colorless which indicated that the organometallic precursor remaining in the solution was reduced as well as the adsorbed precursor on the Black Pearl 2000. After the reduction process, the vessel was depressurized slowly and allowed to cool down. The metal/substrate was taken away from the vessel. For the preparation of Pt-Pd/BP2000 particles, Pt/BP2000 was prepared first. The adsorption of PtCODMe$_2$ on carbon support is the same procedure as the Pd(acac)$_2$/BP2000 preparation but the reduction procedure is different. The reduction of PtCODMe$_2$/BP2000 was carried under H$_2$/N$_2$ atmosphere in an oven at 200 ^{0}C for 4 hours. Then the prepared Pt/BP2000 particles were impregnated with predetermined amount of Pd(acac)$_2$ in scCO$_2$. Afterwards, H$_2$ /scCO$_2$ (PH$_2$= 8 bar, P$_{TOTAL}$= 3000 psi) mixture was injected into the vessel and Pt/BP2000 supported Pd(acac)$_2$ particles were reduced. The metal loading of the composites was measured by using an analytical balance.
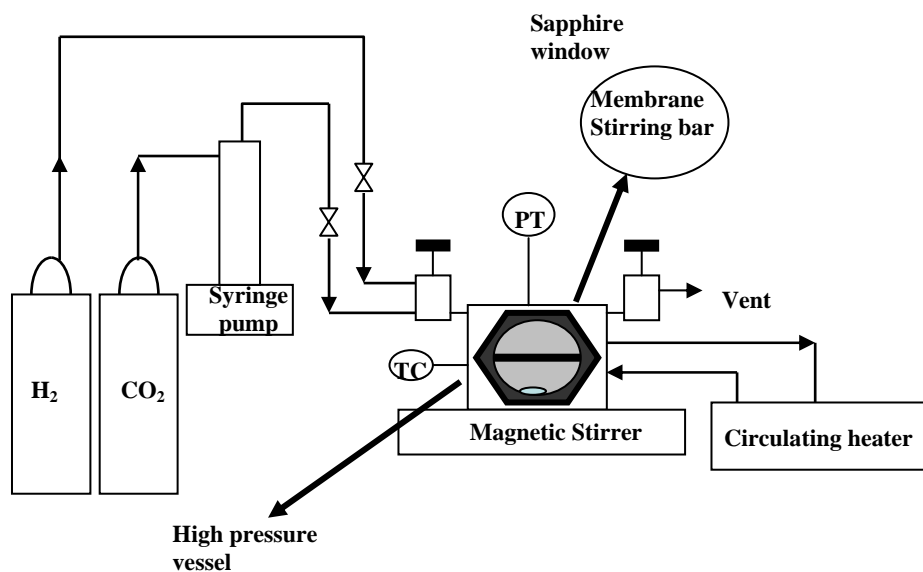
Figure 1. Experimental set-up of the system.

RESULTS

The adsorption isotherm obtained at 3000 psi and 60 ^{0}C is given in Figure 2. The adsorption isotherm is linear in the concentration range of the experiments. The maximum concentration in the fluid phase corresponds to the solubility of the precursor in $scCO_2$ at this condition. Since the solubility of the precursor in scCO2 is very low, the solutions were very dilute in all the experiments leading to a linear behaviour.
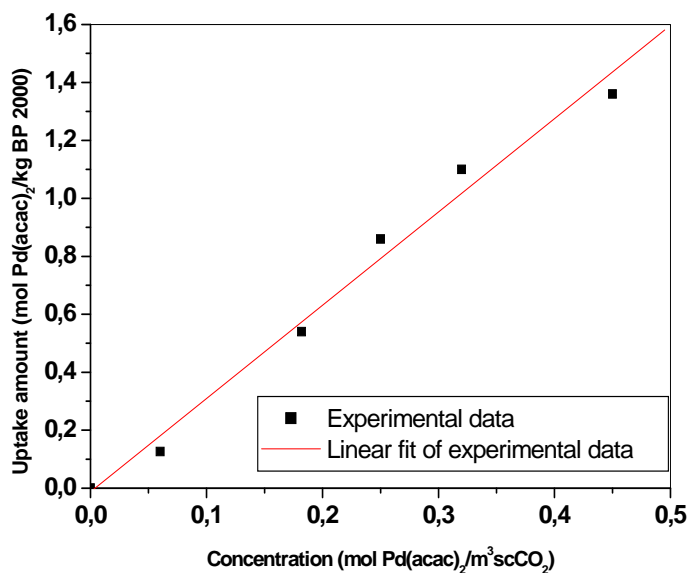

Figure 2. Adsorption isotherm of Pd(acac)$_2$/BP 2000 system at 3000 psi and 60 ^{0}C.

From Figure 2, the relation between the uptake amount of organometallic precursor (A) on substrate (q) and the concentration in supercritical phase (C_A) is given by equation 1:

$$q = 3.22\, C_A \tag{1}$$

Similar to the model given elsewhere [19], a kinetics model for the organometallic palladium (II) acetylacetonate adsorption from scCO$_2$ phase on the carbon support was developed after the determination of the adsorption isotherm shown in Figure 2. Four steps were identified for adsorption from the supercritical phase. These steps were mass transfer of adsorbate from the fluid phase to the adsorbent, diffusion in the pores of the adsorbent, adsorption onto the surface of the adsorbent and surface diffusion within the adsorbent, respectively. First step which is the mass transfer of Pd(acac)$_2$ from scCO$_2$ phase to the carbon can be described by film diffusion which depends on the concentration difference of the bulk scCO$_2$ phase and surface of carbon. Since the solutions were well stirred and perfectly mixed in the experiments, it can be concluded that the concentration of Pd(acac)$_2$ at bulk scCO$_2$ and carbon surface were equal. Therefore, the effect of film diffusion was neglected. In the third step describing adsorption onto the surface, local equilibrium was assumed within the adsorbent where the adsorbed phase concentration was related to the scCO$_2$ concentration through the adsorption isotherm. These assumptions led to the following differential equations:

$$\varepsilon_p \frac{\partial C_A}{\partial t} + \rho_p \frac{\partial q}{\partial t} = D_e \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) \tag{2}$$

The boundary conditions are;

$$\frac{\partial C_A}{\partial r} = 0 \quad \text{at } r = 0 \tag{3}$$

$$-V \frac{\partial C_A}{\partial t} = m \, S \, D_e \frac{\partial C_A}{\partial r} \qquad \text{at } r = R \tag{4}$$

Equation 2 was converted to set of ordinary differential equations and solved. With the solution of these differential equations, the kinetics of adsorption was predicted. The predicted curve is given in Figure 3.
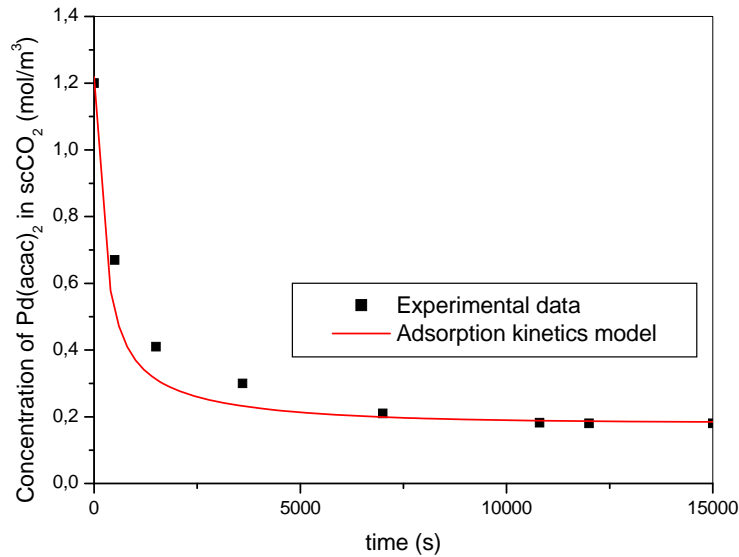

Figure 3. Experimental and model adsorption kinetics curves

The tortuosity value was left as an adjustable parameter in the model and was determined as 1.3. There is very good agreement between the experimental data and the model and the fitting error is %11.2. As can be seen in Figure 3, the system reaches equilibrium approximately in 3 hours.

In the second part of the study, reduction of Pd(acac)$_2$/BP 2000 composites was conducted at 4 different reduction temperatures (50, 60, 70 and 80 ^{0}C) by injecting H$_2$ into solution. Pd loadings of the samples were 20 wt. % by weight. As can be seen in Figure 4, the temperature range used for

reduction in $H_2/scCO_2$ solution did not have a great influence on the particle size. The size of each sample was calculated from the Scherrer equation and they were quite close with an average size of 22 nm.
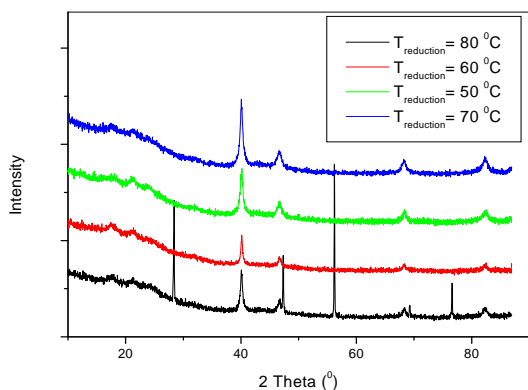

Figure 4. XRD patterns of the Pd/BP 2000 particles formed by reduction at different temperetures in H_2 – $scCO_2$ solution.
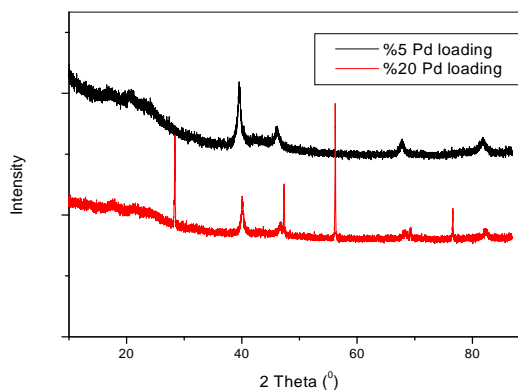

Figure 5. XRD patterns of the Pd/BP 2000 particles at %5 and %20 metal loading at reduction temperature of 80 ^0C in H_2/CO_2 solution.

The effect of the metal content on the particle size was also investigated. As can be seen in Figure 5, when the metal content was reduced to 5 wt. %, the size of the particles also reduced. Both of these experiments were conducted at 80 ^0C in $H_2/scCO_2$ solution. The particle size of the 5% Pd containing sample was 5.2 nm whereas the 20 wt. % Pd containing sample was 23.3 nm.
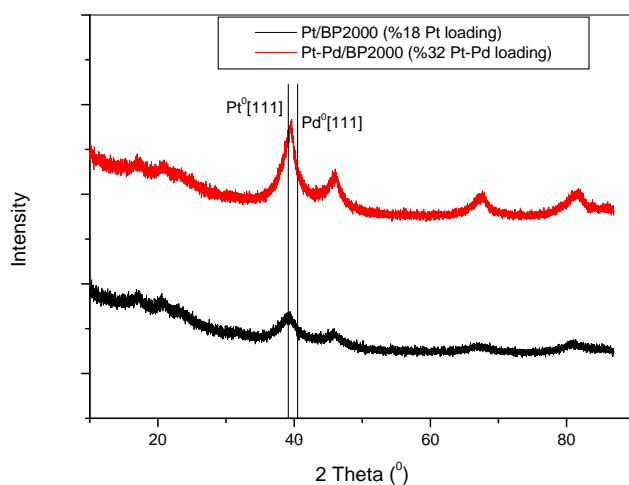

Figure 6. XRD patterns of the Pt/BP2000 with %18 by weight Pt loading and Pt-Pd/BP 2000 with %32 Pt-Pd alloy loading.

The PtPd/BP2000 composites were prepared in the following manner. First, the Pt/BP 2000 composites were obtained by reduction under H_2/N_2 atmosphere at 473 K. The particle size of Pt was 2 nm at a metal loading of 18 wt. %. Subsequently, $Pd(acac)_2$ was impregnated on the Pt/BP2000 particles in $scCO_2$ at 3000 psi and 80 ^0C. Reduction by injecting $H_2/scCO_2$ mixture into this solution led to Pt-Pd alloy formation on BP2000. The particle size of the Pt-Pd alloy calculated from the XRD data presented in Figure 6 was 4.8 nm at 32 wt % total metal loading with a composition of 15 wt % Pt and 17 wt % Pd.

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